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(54) Title: PROCESSING OF POLYHYDROXYALKANOATES USING A NUCLEANT AND A PLASTICIZER

(57) Abstract: The present invention is directed to a polyhydroxyalkanoate copolymer composition that can be readily and quickly processed into extruded and molded articles and film-based products. More specifically, the invention pertains to melt processing of polyhydroxyalkanoates which contain a novel combination of nucleant and plasticizer for enhancing crystallization rates thus causing improved processibility.

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TITLEPROCESSING OF POLYHYDROXYALKANOATES USING
A NUCLEANT AND A PLASTICIZER

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FIELD OF THE INVENTION

This invention relates to the field of polyhydroxyalkanoate polymers, articles made therefrom and melt processing methods. More specifically, the invention pertains to melt processing and cast film extrusion of polyhydroxyalkanoates which contain a novel combination of 10 nucleant and plasticizer for enhancing chain mobility, crystallization rates in order to improve processibility in conventional melt processes.

BACKGROUND OF THE INVENTION

Polyhydroxyalkanoates (PHAs) and other thermoplastic polyesters 15 represent potential raw materials for a myriad of useful products. Examples include melt-spun fibers from which non-woven products can be produced for medical gowns and masks, blown and cast films for compostable grocery and garbage bags, injection-molded bottles for health and personal care products and extrusion coatings on 20 paper/paperboard for biodegradable/compostable fast-food containers. In the processes to produce PHA products, it is crucial to achieve line speeds, cycle times, and other processing parameters that are economically desirable.

Polyhydroxyalkanoate copolymers are extremely sticky when melt 25 processed due, at least in part, to extremely slow crystallization rates of their crystalline phase domains. This sticky or "tacky" behavior leads to an inability to process the polymer through any melt processing equipment, including extrusion, compounding, film and fiber operations. Unmodified polymer has a strong tendency to stick to all pieces of machinery, 30 regardless of the material of construction. The polymer also has a strong tendency to stick to itself and to human skin when touched. The stickiness or tackiness gradually disappears in a matter of minutes to hours. However, this time frame is significantly long for any conventional processing techniques, which generally require the polymer to become 35 non-tacky within a matter of a few seconds.

Previous work has shown that addition of a crystallization nucleant to some compositions of polyhydroxyalkanoate copolymers can increase crystallization rates to a point where melt processibility is acceptable. In

addition, such nucleants can sometimes improve the physical and mechanical properties of the processed articles. Conventional nucleating agents include, for example, talc, micronized mica, calcium carbonate, boron nitride (see, for example, EP 0291024) and ammonium chloride 5 (see, for example, WO 9119759).

U.S. 5,296,521 describes polyester compositions having increased crystallization rates comprising thermoplastic polyester resins and 0.5 to about 5 weight percent of nucleating agent of the formula
RO[P(O)(Ph)(CH₂)_mO]_nH where R is an alkali or alkaline earth metal; m 10 is 1, 2, or 3; n takes an average value within the range of 1 to 5. The nucleating agent can be optionally mixed with the acid or ester form providing at least 50 mole percent of the nucleating agent is in the salt form. The nucleating agent is preferably in the form of the sodium salt (e.g., sodium salt of hydroxymethylphenyl phosphonic acid or sodium salt 15 of oligomethylene phenyl phosphinic acid).

U.S. 4,536,531 describes use of carboxylic salts of metals of Group I and II in the Periodic Table as nucleating agents for polyesters exemplified by metal salts of aliphatic monocarboxylic acids such as acetic acid, propionic acid, caproic acid, palmitic acid, stearic acid, oleic acid, behenic acid and montanic acid. Suitable metals are sodium, potassium, lithium, magnesium, calcium, barium and zinc. In these carboxylic acid salts, it is unnecessary that all the carboxylic groups be converted into salt form, but a part of the carboxyl group may be in a salt form and the remaining groups may be in a free acid or ester form.

Several references disclose the use of organophosphorous 25 compounds as nucleants. U.S. 5,061,743 discloses a preferred polyhydroxyalkanoate nucleant made by dry blending cyclohexylphosphonic acid and zinc stearate with polyhydroxybutyrate-co-valerate. The nucleant is disclosed as particularly advantageous for the 30 nucleation of polyhydroxybutyrate-co-valerate having high hydroxyvalerate content. WO 9905208 discloses that organophosphorous compounds having at least two phosphonic acid moieties can be used as nucleants for polyhydroxyalkanoates and other thermoplastic polyesters.

Although many of these compounds have shown effectiveness in 35 increasing the nucleation density of polyhydroxyalkanoate, and therefore crystallization rates, certain disadvantages have been associated with their use. Dispersion of particulate nucleants, for example, has been problematic because agglomeration frequently occurs during processing

which can generate regions of stress concentration and inhomogeneity in molding. In addition, nucleants such as boron nitride have been found to act as pigments in some situations, particularly in films and injection moldings, giving rise to opaque products where transparent products are
5 generally desired. Further, some nucleant systems include constituents which may be environmentally and toxicologically undesirable.

Furthermore, the polymers of the previous references tend to be copolymers that do not contain a comonomer that effectively increases the amorphous character or decreases crystallization rates of the polymer.
10 The resulting polymers are often brittle and lead to undesirable properties. Polyhydroxyalkanoate copolymers that contain more modifying comonomers, which lead to a significant amount of amorphous phase, tend to be more desirable polymers because they exhibit a high level of toughness and elastic resilience. However, the large amount of
15 amorphous phase contained in these polymers is not conducive to good crystal formation or rapid crystallization rates. Furthermore, addition of nucleants to these polymers generally does not increase the amount of crystallization or the crystallization rate enough to make melt processing of these polymers feasible. Thus, there is a need for benign and cost-
20 effective nucleant systems which allow for the production of polyhydroxyalkanoate resins having moderate to high crystallinity, excellent moldability, mechanical strength and dimensional stability.

The problem to be solved, therefore, is to provide a polymeric composition that produces tough, flexible polyhydroxyalkanoates that can
25 be readily and quickly processed into film-based products. Another objective of this invention is to provide a method for continuous melt extrusion of these polyhydroxyalkanoates. Yet another object of the present invention is to provide a method for continuous cast film production using these polyhydroxyalkanoates.

30

SUMMARY OF THE INVENTION

The invention provides a polyhydroxyalkanoate copolymer composition which can be processed into film-based products, extruded and molded articles, and coatings, comprising: (a) a
35 polyhydroxyalkanoate copolymer; (b) a nucleant; and (c) a plasticizer, and a method of making same.

In a preferred embodiment, unique combinations of either poly-3-hydroxy(butyrate-co-octanoate) or poly-3-hydroxy(butyrate-co-hexanoate)

are polymerized with polyhydroxybutyrate (nucleant) and either methyl laurate or dibutylmaleate (plasticizer).

DETAILED DESCRIPTION OF THE INVENTION

5 Applicants have solved the problem by providing combinations of nucleant and plasticizer to polyhydroxyalkanoate ("PHA") copolymers. Addition of the nucleant and plasticizer to PHA copolymers allows crystallization processes to occur in a time frame which enables practical melt processing. The instant invention is applicable to any situation in
10 which accelerated crystallization rates are desired. In particular, the nucleants and plasticizer are used for improved production of PHA and other thermoplastic polyester products by decreasing the cycle times normally required for producing films, extruded and molded articles, and coatings.

15 In this disclosure, a number of terms and abbreviations are used. The following definitions are provided.

"Poly(3-hydroxybutyrate-co-3-hydroxyoctanoate)" which is also known as "poly-3-hydroxy(butyrate-co-octanoate)" is abbreviated P3HBO.

20 "Poly-3-hydroxy(butyrate-co-hexanoate)" which is also known as "poly-3-hydroxy(butyrate-co-hexanoate)" is abbreviated P3HBH.

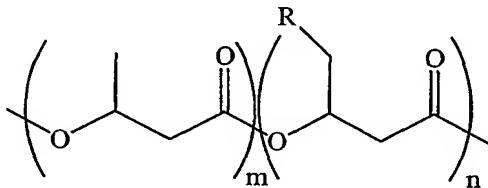
"Polyhydroxyalkanoate" is abbreviated PHA.

"Polyhydroxybutyrate" is abbreviated PHB.

Polyhydroxyalkanoates

25 Polyhydroxyalkanoates ("PHA"s) of this invention include naturally derived polymers such as polyhydroxybutyrate (PHB), including homopolymers of 3-hydroxybutyrate and 4-hydroxybutyrate. They also include copolymers of PHB with hydroxy acids, for example copolymers of PHB with 3-hydroxyhexanoate, 3-hydroxyoctanoate, or longer chain hydroxy acids (e.g. C₉-C₁₂ hydroxy acids) and copolymers thereof. PHAs of this invention can also be synthetically derived from hydroxy carboxylic acids. Furthermore, the PHA can be predominantly of R(-) configuration, predominantly of S(+) configuration, or a random, block, or other combination of R(-) and S(+) configuration. As will be understood by the skilled artisan, the R(-) and S(+) isomers refer to the ability of the repeat 30 unit of the polymer to rotate plane polarized light in the counterclockwise or clockwise direction, respectively. A racemic copolymer consists of both R(-) and S(+) repeat units within the polymer which can be arranged in any combination, including random or block configurations.

Preferred examples of polyhydroxyalkanoate copolymers used in this invention are poly-3-hydroxy(butyrate-co-octanoate) ($y = 3$) (P3HBO)



$$R = \text{CH}_3(\text{CH}_2)_y \text{ where } y = 0 - 11$$

and poly-3-hydroxy(butyrate-co-hexanoate) ($y = 1$) (P3HBH). These block copolymers have the generalized structure shown below.

5

$$m = 0.7-0.97 \text{ and } n = 0.3-0.03, \text{ where } m+n = 1.0$$

- In general, block copolymers can be prepared having various architectures. For example, an A-B diblock copolymer has a block of polymer A segments coupled to a block of B polymer segments. An A-B-A triblock copolymer has a block of B segments coupled to a block of A segments at each of its terminal ends. An $-(A-B)_n-$ multiblock copolymer has alternating sequences of A and B segments where n is a positive integer greater than 1. Especially preferred are random block copolymers in which the PHB segments comprise from 85 to about 95 weight percent of the copolymer. For use in the present invention, PHAs have a weight average molecular weight of about 600,000 to greater than 1,000,000; the number average molecular weight ranges from about 280,000 to 500,000 grams/mole.
- PHAs are generally difficult to process by conventional melt processes into films, fibers, filaments, rods, tubes or other forms having physical integrity. Conventional melt processes include continuous melt extrusion processes, cast film extrusion, blown film extrusion, melt spinning processes and other methods generally known to those skilled in the art. By "polymer difficult to melt process", it is meant that the polymer exhibits an effective melt strength and/or set time that detracts from the ability to form products having physical integrity by a conventional melt extrusion process.
- The "effective melt strength" refers to the resistance of a molten polymer to be drawn-down to a desired dimension such as thickness (in the case of films), or diameter or denier (in the case of fibers or filaments). A polymer having a low effective melt strength is unable to withstand the

minimum strain that is required to draw the polymer melt to a desired dimension. For example, the polymeric material may exhibit instabilities such as breakage, sagging or draw resonance. The resultant products tend to be highly non-uniform in physical integrity.

5 The "set time" refers to the time period required, under a given set of process conditions, for the molten polymer material to achieve a substantially non-tacky or non-sticky physical state. The set time is important because blocking may occur if the polymer does not set within a suitable time during processing. Thus, the polymeric material having
10 residual tack may stick to itself and/or to processing equipment even after cooling to room temperature or below. Such residual tack may restrict the speed at which the product can be processed or prevent the product from being collected in a form of suitable quality.

15 The set time is influenced by the polymer material and the processing equipment and conditions. In general, the set time should be on the order of seconds under conventional process conditions. Such conditions typically include temperatures ranging from that of chill rolls, such as are known in the art, to the melt temperature of the material being processed, which may be up to about 150°C, (preferably 120 to 135 °C).
20 In general, longer process cycle times (e.g. from the point of melt extrusion to the point of take-up of collection) tend to accommodate longer set times.

25 The term "tack" or "tackiness" is known to those skilled in the art to mean sticky or the amount of stickiness. Tack is generally a subjective measurement made by touching the film surface with a finger. If the surface is "tacky", or sticky, then it has the property of "tack". Tack may be measured subjectively by means of many scales, but to illustrate the concept, fly paper may be considered the high point of the scale with a Teflon® sheet (polytetrafluoroethylene) (from E. I. du Pont de Nemours
30 and Company, Wilmington, DE) as having no tack. For the purpose of this invention, tack was subjectively measured by a single operator after pressing a film of the appropriate polymer blend between two sheets of Teflon® coated aluminum foil five times. After the fifth pressing, the sample film was cooled for 10 seconds at room temperature, and the
35 relative force required to first remove the film from the Teflon® sheets was noted. Additionally, the force required to peel the film apart from itself after folding it over on itself was also subjectively monitored along with the force required to peel the polymer from the gloves of the operator. A result of

"no tack" was recorded when no apparent additional force was required to remove the film from the Teflon® sheet or from itself after folding. The subjectively graded scale of "slight tack" to "moderate tack" indicates that more force was required to pull the film from the Teflon® sheet and itself in each respective category. The category of "tacky" indicates that generally the film was extremely difficult to remove from the Teflon® sheet and virtually impossible to separate from itself after folding when cooled under the standard time of 10 seconds.

Nucleants

10 "Nucleants" or "nucleating agents" are compounds used to artificially introduce nucleation sites for the process of polyhydroxyalkanoate crystallization from the molten state. A description is set forth in US Patent No. 5,534,616, starting at column 1, line 36. The reference is hereby incorporated by reference. Nucleants help to
15 compensate for the slow rate of crystallization of many PHAs due to their low nucleation density. The preferred amount of nucleant in the composition is from about 1% to about 10%, based on the total weight of the composition. The nucleant in the preferred composition is polyhydroxybutyrate and is used in an amount ranging from about 0.005%
20 to about 20%, more preferably from about 0.05% to about 10% and most preferably from about 0.5% to about 5%, based on the total weight of the composition.

Plasticizers

25 Plasticizers are used in the instant composition to modify the mechanical properties of products formed and to improve the processability of the composition. In general, a plasticizer tends to lower the modulus and tensile strength, and to increase the ultimate elongation, impact strength, and tear strength of the polymeric product. The plasticizer may also be used to lower the melting point of the composition
30 to thereby enable melt processing at lower temperatures. In this invention the plasticizer is used to lower the glass transition temperature as an aid to increase the rate at which a non-tacky product will be attained.

External plasticizers known in the art include glycerol, ethylene glycol, and low molecular weight polyethylene glycols. Preferred
35 plasticizers for the PHAs examined include di(2-ethylhexyl)(dioctyl)maleate, paraffin, dodecanol, olive oil, soybean oil, polytetramethylene glycols, methyl oleate, n-propyl oleate, tetrahydofurfuryl oleate, epoxidized linseed oil, 2-ethylhexyl epoxytallate,

glycerol triacetate, methyl linoleate, dibutyl fumarate, methyl acetyl ricinoleate, acetyl tri(n-butyl) citrate, acetyl triethyl citrate, tri(n-butyl) citrate, triethyl citrate, bis(2-hydroxyethyl) dimerate, butyl ricinoleate, glyceryl tri-(acetyl ricinoleate), methyl ricinoleate, n-butyl acetyl ricinoleate, propylene glycol ricinoleate, diethyl succinate, diisobutyl adipate, dimethyl azelate, di(n-hexyl) azelate and tri-butyl phosphate.

5 Most preferred plasticizers for the PHAs examined include methyl laurate and di-n-butyl maleate. The preferred amount of plasticizer in the composition is from about 5% to about 35%, and more preferably from

10 about 12% to about 20%, based on the total weight of the composition.

Methods of Melt Extrusion

Conventional melt extrusion methods are used to produce extruded and molded articles of the present invention. Such melt extrusion methods involve blending of polymeric components followed by extrusion

15 of the blend. In a preferred embodiment, the strands of PHA polymer are extruded at about 120-160°C, more preferably from 130-145°C, through the die plate into a water bath having a temperature of about 30-40°C.

In a preferred melt extrusion process of the present invention, pellets of the polymeric components are first prepared. The PHA nucleant and plasticizer can be first dry blended and then melt mixed in the film extruder itself. Alternatively, if insufficient mixing occurs in the melt extruder, the ingredients can be first dry blended and then mixed in a pre-compounding extruder followed by pelletization prior to film melt extrusion.

The PHA films of the present invention may be processed using conventional methods and are used for producing single or multilayer films on conventional film-making equipment. The cast or blown film extrusion methods used to make the PHA films of the present invention are more fully described in US. Patent No. 6,027,787, hereby incorporated by reference, and described in Plastics Extrusion Technology – 2nd Ed., by Allan A. Griff (Van Nostrand Reinhold, 1976). In a preferred embodiment, the PHA polymer continuous film is extruded at about 120-160°C, more preferably from 120-140°C, onto rollers having a temperature of about 30-45°C, more preferably of about 40°C.

“Film” refers to a continuous piece of extruded material having a high length to thickness ratio and a high width to thickness ratio. While there is no requirement for precise upper or lower limits of thickness, a preferred film thickness of the present invention is from about 0.05 to about 50 mil, and a more preferred film thickness is from about 0.5 to

about 15 mil. The films of the present invention can comprise one, two or more layers.

The PHA compositions of the present invention can also be made into certain selected molded articles by conventional injection molding
5 techniques.

EXAMPLES

The present invention is further defined in the following Examples. It should be understood that these Examples, while indicating preferred
10 embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and
15 conditions.

The meaning of abbreviations is as follows: "h" means hour(s), "min" means minute(s), "sec" means second(s), "d" means day(s), "mL" means milliliter(s), "L" means liter(s), "ft" means foot or feet, "lb" means pound(s) and "g" means gram(s).

20 General Methods

Poly-3-hydroxy(butyrate-co-octanoate) (P3HBO) was obtained from Procter and Gamble Company, Inc. (Cincinnati, OH). Poly-3-hydroxy(butyrate-co-hexanoate) (P3HBH) was obtained from Proctor and Gamble Company, Inc. (Cincinnati, OH) (Jiangmen Center for
25 Biotechnology Development and Tsinghua University (China). PHB was supplied by Aldrich Chemical Company, Inc. (St. Louis, MO).

EXAMPLE 1

Identification of "Active" Nucleant and Plasticizer Combinations

Screening of nucleant and plasticizer combinations was conducted
30 as follows: a melt blend of the nucleant PHB and a PHA, specifically, either P3HBO or P3HBH were prepared by first tumble blending powders of the appropriate amounts of PHB and either P3HBO or P3HBH. Generally, 1 wt % PHB (0.75 g) was added to the P3HBO (74.25 g) polymer and 3 wt % PHB (2.25 g) was added to the P3HBH (72.75 g)
35 polymer. (Percent nucleant addition was determined by anti-stick performance in preliminary experiments.) After tumble blending the appropriate ingredients, the powder was fed into a small 16 mm PRISM twin screw extruder set to a maximum temperature of 155°C. The

polymer was melt extruded through a single hole 3/16-inch die into a water bath and onto a water-cooled "non-stick" belt. The polymer tended to stick to the belt and was cut into 2 to 3 ft lengths and draped over a rack to allow time for crystallization to occur. After 20 min to 1 hr, the polymer strands had crystallized sufficiently to be hand cut with scissors or run through a blade cutting machine to produce small (2 to 8 mm long) pellets. The pellets were then pressed into film under the following conditions: press temperature (140°C); pressure (1000 psi); minutes in press (2 min); cooling temperature (25°C). The resulting film was then cut into 2 to 5 mm wide strips to be used in the screening process.

Because good mixing facilities were not available for blending very small quantities of polymer and plasticizer, the following methodology was developed and followed to screen melt blends of polymer, nucleant and plasticizer. Into a small test tube was added 0.4 g of the desired plasticizer. The test tube containing the plasticizer was placed into a Wood's metal bath heated to 160°C and held there for 10 min. After the plasticizer was pre-heated, 1.6 g of the appropriate PHA film strips containing the PHB nucleant (prepared as described above) were added to the test tube. The entire content of the tube was then heated at 160 °C for an additional 50 min. The tube was then removed from the heating bath and allowed to cool at room temperature for at least 1 h. The resulting polymer blend was removed from the test tube (breaking the tube if necessary). The resulting polymer and any liquid contents were put onto a Teflon® coated aluminum foil sheet (commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE) and pressed into a film. The film was then removed from the sheet, folded over onto itself and pressed again into a film. The film pressing process was repeated 5 times to ensure good blending of the three ingredients and to evaluate the effectiveness of the nucleant plasticizer combination. Film processing conditions were generally as follows: press temperature (140°C); press pressure (1000 psi); press time (2 min); cool temperature (room temperature); cool pressure (5 lb plate); and cool time (10 sec). Immediately after the final film was pressed and cooled for 10 sec, the sample was peeled from the Teflon® coated sheet and evaluated for tack to the Teflon® coated sheet, to itself, and to the operator's gloves. If the sample exhibited no stickiness or tackiness, as defined herein, to any of the surfaces to which it was exposed, it was given a rating of "no tackiness". All other ratings indicate some level of tack. The sample was

then wiped of any remaining plasticizer and weighed. Percent incorporation of plasticizer was determined by comparing final polymer weight to theoretical weight and back calculating plasticizer content assuming only plasticizer loss. A sample calculation follows:

5 Ingredients added:

1.6 g (nucleant + polymer) as film
0.4 g plasticizer

Total ingredients processed = 1.60 g + 0.40 g = 2.00 g

Theoretical % plasticizer = (0.40 g / 2.00 g) x 100% = 20%

10 General example:

Actual final weight of film = X g

Assumed final weight of plasticizer = X g - 1.60 g = Y g

Actual % plasticizer = (Y g / X g) x 100%

Specific example:

15 Actual final weight of film = 1.86 g

Assumed final weight of plasticizer = 1.86 g - 1.60 g = 0.26 g

Actual % plasticizer present = (0.26 g / 1.86 g) x 100% = 14%

It should be noted that in no case was a film of less than 1.60 g ever produced, indicating that in all cases some plasticizer was incorporated into the polymer.

20 Table 1 (examples 1-44) summarizes the nucleant and plasticizer screening done with both P3HBO and P3HBH, respectively, that showed results of no tack. Table 2 (examples 45-60) summarizes comparative examples that do exhibit tack. The abbreviation Tg used in Table 1 and 25 Table 2 represents glass transition temperature (°C);

25 In general, for those samples that produced a rating of "no tackiness", the samples that retained more plasticizer tended to perform better (show even less tack) than those that retained less plasticizer.

Occasionally, tack was still evident when some films were cooled at room

30 temperature. If these same films were cooled at 65°C, some of them then exhibited no tack. These films were given a rating of no-tack; however, they are considered inferior to those that exhibit no tack after 10 sec of room temperature cooling. The samples that exhibit rapid elimination of tack were considered to be candidates for melt processing via injection 35 molding, film extrusion and fiber extrusion.

EXAMPLE 2Demonstration of Continuous Melt Extrusion of Poly-3-hydroxy(butyrate-co-hexanoate) into Strand and On-line Pelletizing

Blending of Ingredients (di-n-butylmaleate plasticizer): Into a

5 35 gallon fiberpak was added 15088.6 g of powdered P3HBH, and 588.5 g of powdered PHB. To this powder mixture was slowly added 3923.0 g of di-n-butylmaleate at such a rate that the liquid plasticizer was immediately imbibed into the powder. The fiberpak was then placed onto a barrel tumbler and tumbled for six h to ensure good mixing.

10 Extrusion of Polymer Strand and Pelletizing (di-n-butylmaleate plasticizer): After tumbling the polymer ingredients as described, the resulting mixture was fed into a 30 mm twin screw extruder at a rate of approximately 10 lb/h. The extruder temperatures were set to maintain a gradient barrel temperature of 120 °C to 160 °C. Screw RPM was

15 maintained at 100. The resulting molten polymer was extruded through a 3/16 inch die into a 12-foot long water trough kept at a temperature of 34 °C to 38 °C. The polymer was cut at a rate of 6 to 8 ft/min and fed directly into a Conair polymer cutter. A total of 40.9 lb of pellets were collected.

20 The resulting polymer strand exhibited some tacky behavior within the first 6 feet of the quench trough. After the strand became non-tacky in the water trough, the polymer exhibited no tacky behavior at any time during the processing operation or in subsequent processing operations.

EXAMPLE 3Demonstration of Continuous Melt Extrusion of Poly-3-hydroxy(butyrate-co-hexanoate) into Strand and On-line Pelletizing

Blending and Extrusion of Polymer Strand and Pelletizing (methyl laurate plasticizer): In a process similar to that described for polymer blended with di-n-butylmaleate in Example 2, the following ingredients 30 were blended: 11,793 g of P3HBH, 459.5 g of PHB, and 3063 g of methyl laurate. The resulting mixture was then fed into a 30 mm extruder as previously described set to maintain a gradiated barrel temperature between 120 °C to 160 °C. The screw RPM was maintained at 100 and polymer was extruded through a 3/16 inch die into a 12-foot water trough 35 maintained at 34 °C to 38°C. The polymer was cut at a rate of approximately 12 ft/min by a Conair polymer cutter. The polymer quench time (the time at which no further tackiness was observed) was approximately 25 sec. A total of approximately 32 lb of non-tacky pellets

were collected. It was noted that methyl laurate promoted faster quench times, thus allowing faster cutting rates.

EXAMPLE 4

Demonstration of Continuous Cast Film Production Using

5 Poly-3-hydroxy(butyrate-co-hexanoate) with Methyl Laurate Plasticizer

- P3HBH pellets plasticized with methyl laurate and nucleated with PHB as prepared in the previous examples were fed into a single screw extruder equipped with a 14 inch film die and set to maintain a gradiated barrel / die temperature of 140 °C to 120 °C. The resulting polymer
 10 extrudate was cast onto 12 inch diameter stainless steel rolls set at a temperature of 40 °C. The extruded film was taken up onto the quench rolls and then onto packaging rolls at speeds ranging from 2 ft/min to 13 ft/min to produce films of thicknesses ranging from 1 mil to 10 mil. The film exhibited no tack and the following properties summarized in Table 3,
 15 (measured according to ASTM D 882-95a - Standard Test Method for Tensile Properties of Thin Plastic Sheeting):

Table 3

Direction	Thickness (mil)	Young's Mod. (MPa)	Strain at Break (%)	Stress at Break (MPa)	Toughness (J/in ³)
Machine	1.7	187	562	10.3	745
Cross	1.7	147	524	8.2	623

20

Table 1

EX. #	COMPOSITION (+ NUCLEANT)	PLASTICIZER	WT% PLASTICIZER	FILM QUALITY
1	PHBO / PHB (99:1)	di(2-ethylhexyl)(dioctyl)maleate	12	no tackiness
2	PHBO / PHB (99:1)	paraffin	3.6	no tackiness
3	PHBO / PHB (99:1)	dodecanol	7	no tackiness
4	PHBO / PHB (99:1)	polyethylene glycol 600	7	no tackiness
5	PHBO / PHB (99:1)	polyethylene glycol 8000	11	no tackiness
6	PHBO / PHB (99:1)	olive oil	2.4	no tackiness
7	PHBO / PHB (99:1)	soybean oil	4.8	no tackiness
8	PHBO / PHB (99:1)	TERETHANE 650	14	no tackiness
9	PHBO / PHB (99:1)	methyl oleate	14	no tackiness
10	PHBO / PHB (99:1)	n-propyl oleate	12	no tackiness
11	PHBO / PHB (99:1)	tetrahydrofurfuryl oleate	13	no tackiness
12	PHBO / PHB (99:1)	epoxidized linseed oil	9	no tackiness
13	PHBO / PHB (99:1)	2-ethylhexyl epoxyalate	11	no tackiness
14	PHBO / PHB (99:1)	dibutyl fumarate	20	no tackiness
15	PHBO / PHB (99:1)	glycerol triacetate	18	no tackiness
16	PHBO / PHB (99:1)	methyl laurate	12	no tackiness
17	PHBO / PHB (99:1)	methyl linoleate, 75%	9	no tackiness
18	PHBO / PHB (99:1)	di-n-butyl maleate	17	no tackiness
19	PHBO / PHB (99:1)	methyl acetyl ricinoleate	11	very good
20	PHBO / PHB (99:1)	acetyl tri(n-butyl) citrate	19	very little tack

EX. #	COMPOSITION (+ NUCLEANT)	PLASTICIZER	WT% PLASTICIZER	FILM QUALITY
21	PHBO / PHB (99:1)	acetyl triethyl citrate	20	very little tack
22	PHBO / PHB (99:1)	tri(n-butyl) citrate	20	very little tack
23	PHBO / PHB (99:1)	triethyl citrate	20	very little tack
24	PHBO / PHB (99:1)	bis(2-hydroxyethyl) dimerate	7	very little tack
25	PHBO / PHB (99:1)	butyl ricinoleate	19	OK
26	PHBO / PHB (99:1)	glyceryl tri-(acetyl ricinoleate)	6	OK
27	PHBO / PHB (99:1)	methyl ricinoleate	18	OK
28	PHBO / PHB (99:1)	n-butyl acetyl ricinoleate	13	OK
29	PHBO / PHB (99:1)	propylene glycol ricinoleate	17	OK
30 (control)	PHBO / PHB (99:1)			high tack
31	PHBH / PHB (97:3)	paraffin	2.4	no tackiness
32	PHBH / PHB (97:3)	dodecanol	8	no tackiness
33	PHBH / PHB (97:3)	dibutyl fumarate	17	non stick
34	PHBH / PHB (97:3)	methyl laurate	18	non stick
35	PHBH / PHB (97:3)	methyl linoleate	17	non stick
36	PHBH / PHB (97:3)	di-n-butyl maleate	19	non stick
37	PHBH / PHB (97:3)	methyl ricinoleate	18	non stick
38	PHBH / PHB (97:3)	diethyl succinate	17	non sticky
39	PHBH / PHB (97:3)	diisobutyl adipate	19	non tacky
40	PHBH / PHB (97:3)	dimethyl azelate	19	non tacky
41	PHBH / PHB (97:3)	di(n-hexyl) azelate	17	non tacky
42	PHBH / PHB (97:3)	tri-butyl phosphate	20	non-tacky

EX. #	COMPOSITION (+ NUCLEANT)	PLASTICIZER	WT% PLASTICIZER	FILM QUALITY
43	PHBH / PHB (97:3)	di(2-ethylhexyl)(diocetyl)maleate	17	OK
44	PHBH / PHB (97:3)	TERETHANE 650	15	OK

Table 2

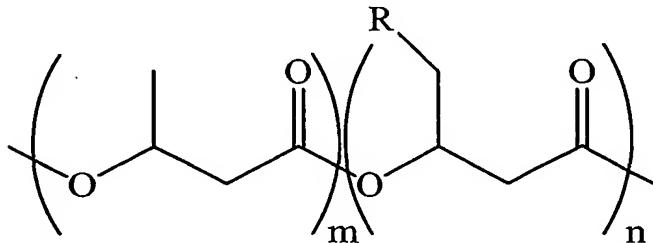
EX. #	COMPOSITION (+ NUCLEANT)	PLASTICIZER	WT% PLASTICIZER	FILM QUALITY
45	PHBO - CONTROL			tacky
46	PHBH - CONTROL			tacky
47	PHBH / PHB (97:3)			tacky
48	PHBO / PHB (97:3)			tacky
49	PHBO/MICROCRYSTALLINE CELLULOSE (97:3)			tacky - removed easily from teflon when hot - tacky as it cooled
50	PHBO/NUCREL 1214 (95:5)			tacky
51	PHBO/paraffin (95:5)			worse than control
52	PHBO/PO2G (95:5)			tacky
53	PHBO/POLYETHYLENE GLYCOL 8000 (97:3)			slightly tacky
54	PHBO/POLYLACTIC ACID (97:3)			tacky
55	PHBO/SURLYN 8020 (95:5)			tacky
56	PHBH / PHB (97:3)	butyl oleate	8	tacky
57	PHBH / PHB (97:3)	dinitidecyl adipate	15	slightly tacky
58	PHBH / PHB (97:3)	dodecanol	8	slightly tacky

EX. #	COMPOSITION (+ NUCLEANT)	PLASTICIZER	WT% PLASTICIZER	FILM QUALITY
59	PHBH / PHB (97:3)	epoxidized linseed oil	13	slightly tacky
60	PHBH / PHB (97:3)	olive oil	2	slightly tacky
61	PHBH / PHB (97:3)	soybean oil	3	tacky
62	PHBH / PHB (97:3)	triethyl citrate	18	tacky
63	PHBO / PHB (99:1)	chloroparaffin, 50% Cl	9	tacky
64	PHBO / PHB (99:1)	n-butyI stearate	6	some tackiness

CLAIMS

What is claimed is:

1. A polyhydroxyalkanoate polymer composition with reduced tack, comprising,
 - 5 (a) a polyhydroxyalkanoate copolymer,
 - (b) a nucleant, and
 - (c) a plasticizer.
2. A polyhydroxyalkanoate polymer composition with reduced tack, comprising,
 - 10 (a) 55-94% polyhydroxyalkanoate copolymer,
 - (b) 1-10% nucleant, and
 - (c) 5-35% plasticizer.
3. The polyhydroxyalkanoate polymer composition of Claim 1



Formula I

$$R = CH_3(CH_2)_y \text{ where } y = 0 - 11$$

wherein the polyhydroxyalkanoate copolymer is selected from compounds having Formula I, wherein $m = 0.7-0.97$, $n = 0.3-0.03$, and wherein $m+n = 1.0$.

4. The polyhydroxyalkanoate polymer composition of Claim 1 wherein the polyhydroxyalkanoate copolymer is selected from the group consisting of poly-3-hydroxy(butyrate-co-octanoate) and poly-3-hydroxy(butyrate-co-hexanoate).
5. The polyhydroxyalkanoate polymer composition of Claim 1 wherein the nucleant is polyhydroxybutyrate.
6. The polyhydroxyalkanoate polymer composition of Claim 1 wherein the nucleant is selected from the group consisting of talc, micronized mica, calcium carbonate, boron nitride, ammonium chloride, sodium salts, and carboxylic salts of metals of Group I and II of the Periodic Table.

7. The polyhydroxyalkanoate polymer composition of Claim 1 wherein the plasticizer is selected from the group consisting of di-n-butyl maleate, methyl laureate, dibutyl fumarate, di(2-ethylhexyl) (dioctyl) maleate, paraffin, dodecanol, olive oil, soybean oil, polytetramethylene glycols, methyl oleate, n-propyl oleate, tetrahydofurfuryl oleate, epoxidized linseed oil, 2-ethyl hexyl epoxytallate, glycerol triacetate, methyl linoleate, dibutyl fumarate, methyl acetyl ricinoleate, acetyl tri(n-butyl) citrate, acetyl triethyl citrate, tri(n-butyl) citrate, triethyl citrate, bis(2-hydroxyethyl) dimerate, butyl ricinoleate, glyceryl tri-(acetyl ricinoleate), methyl ricinoleate, n-butyl acetyl ricinoleate, propylene glycol ricinoleate, diethyl succinate, diisobutyl adipate, dimethyl azelate, di(n-hexyl) azelate and tributyl phosphate.
8. A method of improving the processibility of a polyhydroxyalkanoate polymer composition by reducing tack, the method comprising the step of contacting polyhydroxyalkanoate polymer with a nucleant and a plasticizer to form a polyhydroxyalkanoate polymer composition.
9. The method according to Claim 8, further comprising the step of extruding the polyhydroxyalkanoate polymer composition.
10. The method according to Claim 9, further comprising the step of pelletizing the extruded polyhydroxyalkanoate polymer composition.
11. The method according to Claim 10, further comprising the step of extruding the pelletized polyhydroxyalkanoate polymer composition.
12. The method according to Claim 10, wherein the polyhydroxyalkanoate polymer composition is extruded through a compound extruder.
13. An extruded article comprising the polyhydroxyalkanoate polymer composition of Claim 1.
14. The extruded article of Claim 13 in the form of a fiber, filament, rod, tube or cast film.
15. The cast film of Claim 14 having a film thickness from about 0.05 to about 50 mil.
16. The cast film of Claim 14 having a film thickness from about 0.10 to about 15 mil.
17. An extruded article produced by the method of Claim 8.
18. An extruded article produced by the method of Claim 9.
19. An extruded article produced by the method of Claim 11
20. An extruded article produced by the method of Claim 12.

21. An extruded article produced by the method of Claim 8 in the form of a fiber, filament, rod, tube, or cast film.
22. An extruded article produced by the method of Claim 9 in the form of a fiber, filament, rod, tube, or cast film.
5
23. An extruded article produced by the method of Claim 11 in the form of a fiber, filament, rod, tube, or cast film.
- 10 24. An extruded article produced by the method of Claim 12 in the form of a fiber, filament, rod, tube, or cast film.
- 15 25. An injection molded article comprising the polyhydroxyalkanoate polymer composition of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/12541

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L67/04 C08K5/00 C08K3/00 C08K13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 05208 A (MONSANTO CO) 4 February 1999 (1999-02-04) cited in the application page 1, line 5 - line 9 page 3, line 24 - line 32 page 5, line 3 - line 21 page 6, line 29 -page 7, line 12 page 12, line 19 - line 26 examples 3,9 ---	1-25
X	EP 0 291 024 A (PERSONAL PRODUCTS CO) 17 November 1988 (1988-11-17) cited in the application page 2, line 4 - line 5 page 2, line 42 - line 50 page 4, line 16 - line 40 claim 8; examples ---	1-25 -/-

Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search 25 July 2002	Date of mailing of the international search report 07/08/2002
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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 02/12541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 550 173 A (HAMMOND TIMOTHY ET AL) 27 August 1996 (1996-08-27) column 1, line 3 - line 4 column 1, line 24 - line 34 column 1, line 59 - line 61 column 2, line 9 - line 45 column 3, line 45 - line 48 column 4, line 66 -column 5, line 13; examples 6,8,9; table 7 ---	1-25
A	MANSOUR A A ET AL: "II. Dielectric investigation of cold crystallization of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V., GB, vol. 40, no. 19, September 1999 (1999-09), pages 5377-5391, XP004167777 ISSN: 0032-3861 the whole document ---	1-25
X	US 5 693 389 A (LIGGAT JOHN JAMIESON) 2 December 1997 (1997-12-02) column 1, line 5 - line 6 column 1, line 22 - line 27 column 1, line 38 - line 43 column 2, line 9 - line 51 column 3, line 65 -column 4, line 57 column 5, line 3 - line 9 example 4 ---	1-25
X	WO 99 23161 A (MONSANTO CO) 14 May 1999 (1999-05-14) page 1, line 4 - line 6 page 2, line 24 -page 5, line 25 page 13, line 3 -page 14, line 2 claims; examples ---	1-25
X	US 5 789 536 A (LIGGAT JOHN JAMIESON ET AL) 4 August 1998 (1998-08-04) column 1, line 24 - line 31 column 2, line 13 - line 56 column 3, line 31 -column 4, line 36 column 5, line 15 - line 25 examples 1-3 ---	1-25
A	US 5 618 855 A (NODA ISAO) 8 April 1997 (1997-04-08) the whole document ---	1-25
		-/-

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/12541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 516 825 A (MONTADOR HENRY J ET AL) 14 May 1996 (1996-05-14) column 1, line 3 - line 6 column 1, line 15 - line 58 column 2, line 45 -column 3, line 10 examples ---	1-25
X	US 5 231 148 A (REICHERT KARL-HEINZ ET AL) 27 July 1993 (1993-07-27) column 1, line 9 - line 15 column 1, line 46 - line 66 column 2, line 4 - line 11 column 2, line 63 -column 3, line 43 column 4, line 57 - line 68 examples 2,7 ---	1-10
A	DATABASE WPI Week 9920 Derwent Publications Ltd., London, GB; AN 1999-232811 XP002207525 & JP 11 060917 A (MITSUBISHI GAS CHEMICAL) abstract	1-25
A	& PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 060917 A abstract ---	1-25
X	WO 99 23146 A (MONSANTO CO) 14 May 1999 (1999-05-14) page 1, line 4 - line 7 page 3, line 16 -page 4, line 2 page 5, line 22 -page 7, line 30 page 9, line 16 -page 10, line 3 page 10, line 17 -page 21, line 2 page 23, line 7 -page 26, line 27; claims; examples -----	1-25

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/12541

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9905208	A	04-02-1999	AU EP WO US	8758498 A 0996671 A1 9905208 A1 5973100 A		16-02-1999 03-05-2000 04-02-1999 26-10-1999
EP 0291024	A	17-11-1988	US AT AU AU BR CA DE DE EP ES GR IE JP JP KR NZ PH PT ZA ZW	4900299 A 102001 T 620805 B2 1581488 A 8802273 A 1306834 A1 3888014 D1 3888014 T2 0291024 A2 2061549 T3 88100301 A , B 62839 B 2703558 B2 63302845 A 9707093 B1 224439 A 27307 A 87455 A , B 8803306 A 5688 A1		13-02-1990 15-03-1994 27-02-1992 17-11-1988 06-12-1988 01-09-1992 07-04-1994 06-10-1994 17-11-1988 16-12-1994 23-02-1989 08-03-1995 26-01-1998 09-12-1988 02-05-1997 21-12-1989 28-05-1993 31-05-1989 31-01-1990 22-11-1989
US 5550173	A	27-08-1996	AU AU CA EP FI WO JP NO	684499 B2 6396294 A 2147982 A1 0668893 A1 952163 A 9411445 A1 8503723 T 951749 A		18-12-1997 08-06-1994 26-05-1994 30-08-1995 05-05-1995 26-05-1994 23-04-1996 04-05-1995
US 5693389	A	02-12-1997	AU AU CA EP FI WO JP NO	683466 B2 6727594 A 2162173 A1 0700418 A1 955645 A 9428070 A1 8510498 T 954748 A		13-11-1997 20-12-1994 08-12-1994 13-03-1996 23-11-1995 08-12-1994 05-11-1996 23-11-1995
WO 9923161	A	14-05-1999	AU EP WO US	1123099 A 1027384 A2 9923161 A2 6191203 B1		24-05-1999 16-08-2000 14-05-1999 20-02-2001
US 5789536	A	04-08-1998	AU CA EP WO JP	6851394 A 2163552 A1 0701580 A1 9428047 A1 8510293 T		20-12-1994 08-12-1994 20-03-1996 08-12-1994 29-10-1996
US 5618855	A	08-04-1997	US US US	5685756 A 5747584 A RE36548 E		11-11-1997 05-05-1998 01-02-2000

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/12541

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
US 5618855	A		US 5498692 A US 5489470 A US 5602227 A AU 1056895 A AU 730347 B2 AU 9820098 A BR 9408512 A CA 2181791 A1 CN 1142839 A CZ 9602192 A3 EP 0739368 A1 FI 962997 A HU 75180 A2 JP 9508423 T NO 963104 A NZ 276325 A PL 315691 A1 RU 2137784 C1 SG 49114 A1 SK 97096 A3 TW 383316 B WO 9520614 A1 US 5780368 A ZA 9500627 A	12-03-1996 06-02-1996 11-02-1997 15-08-1995 08-03-2001 04-03-1999 04-03-1997 03-08-1995 12-02-1997 11-12-1996 30-10-1996 26-07-1996 28-04-1997 26-08-1997 27-09-1996 28-07-1998 25-11-1996 20-09-1999 18-05-1998 09-04-1997 01-03-2000 03-08-1995 14-07-1998 05-10-1995
US 5516825	A	14-05-1996	AT 160371 T AU 676191 B2 AU 4723893 A CA 2142333 A1 DE 69315345 D1 DE 69315345 T2 DK 655077 T3 EP 0655077 A1 ES 2109677 T3 FI 950593 A WO 9404607 A1 JP 8502085 T NO 950522 A	15-12-1997 06-03-1997 15-03-1994 03-03-1994 02-01-1998 09-04-1998 22-12-1997 31-05-1995 16-01-1998 10-02-1995 03-03-1994 05-03-1996 10-02-1995
US 5231148	A	27-07-1993	AT 258390 A AT 176917 T DE 59109103 D1 EP 0491171 A2 JP 4314726 A	15-08-1997 15-03-1999 01-04-1999 24-06-1992 05-11-1992
JP 11060917	A	05-03-1999	NONE	
WO 9923146	A	14-05-1999	AU 1281499 A EP 1025152 A1 WO 9923146 A1 US 6127512 A	24-05-1999 09-08-2000 14-05-1999 03-10-2000

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